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Adsorptive removal of methylene blue from aqueous solutions with activated carbon from agricultural waste material: *Irvingia Gabonensis* seed shell

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ABSTRACT

The application of low cost, available and eco-friendly adsorbents has been investigated as an ideal alternative to the current expensive methods of removing dyes from wastewater. The use of activated carbon prepared from *Irvingia Gabonensis* for the removal of methylene blue from simulated effluent water has been studied. The contact time results showed that equilibrium was attained at 100 minutes and that the smaller-sized adsorbents were more efficient in removing colour from effluent water than the large-sized adsorbents. The equilibrium sorption fitted into the Langmuir and Freundlich adsorption isotherms. Thus activated carbon from *Irvingia Gabonensis* can be an attractive option for the removal of dyes from diluted industrial effluents.

KEYWORDS

Adsorption;
Irvingia Gabonensis;
Activated carbon;
Methylene blue.

INTRODUCTION

Synthetic dyes have been extensively discharged into the environment from different industries, particularly textile, paper, rubber, plastic, leather, food and drug industries which use synthetic dyes in coloring their products. It has been reported that over 100,000 commercially available dyes exist and the global annual production of synthetic dyes has been estimated to be more than 700,000 metric tonnes[1]. The discharge of dye waste water into environmental water bodies deteriorates the water quality by causing considerable variation in water quality parameters like pH, chemical oxygen demand (COD) and biological oxygen demand (BOD), and this may have some significant health implications on both aquatic and human life, due to the toxic, carcinogenic, mutagenic, and or teragenic effects of some of these dyes and their metabolites[2].

Different physical, chemical and biological processes have been employed for the treatment of dye contaminated waste water[3]. Some electrochemical and ion-pair extraction methods are presently being used for textile waste treatment[4], while chemical precipitation, biological and photo-catalytic oxidation have been found to be effective in colour removal[5]. In all these methods, adsorption on activated carbon has been found to be superior due to its economical and effective dye waste water treatment. Activated carbon is commonly defined as a carbonaceous material showing a well-developed surface area and porous texture[6]. Though

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the removal of dyes through activated carbon sorption is quite effective, the large scale application is restricted due to its higher cost and regeneration problems[7] as well as scarce selectivity[6], the latter of which is improved by the variation of production procedure. At present, there is a growing interest in the use of low cost[8] commercially available materials for the adsorption of dyes from aqueous solution. A wide variety of materials such as coir pith[9], sunflower stalks[10], corncob and bailey husk[11], rice husk[12], kohlrabi peel[13] ricinus communis epicarp[14], activated clay[15], almond shell[16] and goat hair[17], etc, have been investigated as low cost sorbents for the reactive dye removal from industrial effluents. Some other workers like Pollard et al.[18], Mall et al.[19], and Bailey et al.[20], have equally reviewed critically various cost efficient adsorbents for waste and waste water treatment.

This work investigates the possibility of using activated carbon prepared from *Irvingia Gabonensis* seed shell, a local agricultural waste material for the removal of methylene blue from simulated dye polluted water.

Methylene Blue, MB, is a thiazine (cationic) dye, which is most commonly used for coloring paper, temporary hair colorant, dyeing cottons, wools and so on. Although MB is not considered to be a very toxic dye, it can reveal very harmful effects on living things[21]. After inhalation, symptoms such as difficulties in breathing, vomiting, diarrhea and nausea can occur in humans[22].

MATERIALS AND METHODS

Adsorbate

Commercial quality methylene blue (Sigma Aldrich make) was obtained and used without any further purification. Zinc chloride ($ZnCl_2$) from Merck Scientific Company was also used.

Absorbents

The shell of *Irvingia Gabonenses* was obtained from the Green House area of the University of Nigeria, Nsukka and taken to the Department of Botany herbarium for identification.

Production of activated carbon

The shells of *Irvingia Gabonenses* obtained were prepared according to the methods of Okoye at al.[23]. The shells were peeled to remove the endocarp, dried in the oven at 80^{0}C for 2h. and cleaned to remove the fibre still remaining on the surface of the shell. The shell so obtained was washed with distilled water, dried, pulverized and sieved to obtain three mesh sizes of the adsorbents; 0.5mm, 1.0mm and 2.0mm.

Activation and carbonization

The activation and carbonization processes were performed according to a method adapted by Ochonogor and Ejikeme[24]. Concentrated solutions of zinc chloride were prepared by dissolving 50g of zinc chloride crystals with distilled water in a 1000ml beaker. 50g of 0.5mm sized carbon material was added to the zinc chloride solution and the resulting mixture was boiled for about 60 minutes in the beaker using an electric heater. The content of the beaker was emptied into a porcelain tray and dried at 120^0 C in an oven. The dried carbon material was then put in a crucible and carbonized in a multiple furnace at 650^{0}C under inert atmosphere. The resulting active carbon was washed with 10% HCl, rinsed with distilled and then deionized water, dried and stored in a dissicator for use. This procedure was repeated for the 1.0mm and 2.0mm sized carbons respectively.

Preparation of standard methylene blue solution

0.032g of the solid dye (Figure 1) was weighed using a Metler electronic weighing balance and placed in a one litre volumetric flask, shaken vigorously to bring about dissolution before the solution was made up to the mark with distilled water. A small quantity of the solution was further diluted and scanned using a spectrophotometer to obtain the wavelength of maximum absorption of the methylene blue using a UNICO-20 spectrophotometer at 625nm.

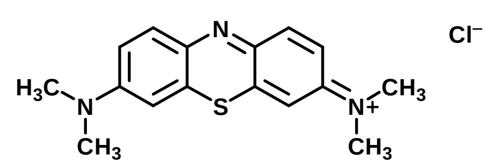

Figure 1 : Structure of methylene blue dye

Characterization of adsorbents

Determination of ash content

The ash content of the adsorbent was determined using the method according to ASTM D 2866[25]. A weighed sample of the adsorbent was pre-dried at 150°C, burnt in a muffle furnace at 650°C for 4 hours in the presence of air. The ash content was calculated from the combustion residue after repeated experiment that led to constant ash content, as follows:

$$\% \text{ Ash content} = W_a/W_b \times 100 \quad (1)$$

where, W_a is the weight of dry ash (g) and W_b is the weight of dry adsorbent (g). An average of four replicates was taken.

Contact time determination

This experiment was carried out using 2g of each of the three mesh sized adsorbents by weighing and transferring them into a 200cm^3 solution of meltylene blue of concentrations 32, 16, 8 and 4mglit^{-1}. It was consecutively stirred with a magnetic stirrer at a constant speed of 200rpm for all the different systems of activated carbon in the standard dye. Aliquots of the solution were drawn out at 1, 2, 3, 4, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90 and 100 minutes interval from the start of the experiment and the respective absorbance's of all the different samples taken. A contact time data was gotten at a spectrophotometric wavelength of 625nm.

Isotherm studies

For a sample of mesh size 2.0mm of activated carbon, masses of 0.5g, 1.0g, 1.5g, 2.0g an 2.5g were measured out and each were contacted with 50cm^3 of 0.031125g/dm^3 solution of melthylene blue for 180 minutes (over this time interval, equilibrium was achieved) at room temperature of 27^{0}C. The concentrations of the various solutions were measured and the fractions adsorbed against equilibrium concentration obtained for each of the activated carbon sample. The average of three absorbance measurements was recorded. This procedure was repeated for 0.5 and 1.0 mesh sizes respectively.

RESULTS AND DISCUSSION

Ash content

Ash content is the indicator of the quality of an activated carbon. It is the residue that remains when carbonaceous portion is burned off. The ash consists mainly of minerals such as silica, aluminum, iron, magnesium, and calcium. Ash in activated carbon is not desirable and is considered an impurity[26]. Granulated activated carbon from sugarcane bagasse with beet and cane molasses as binding agents have been reported to have 57.57 and 42.74% ash giving 9.04 and 7.17% removal of colour respectively from sugar while a commercial carbon gave 15-18% removal in the same study[27].

Effect of contact time

Figures 2-5 shows the plots of concentration of methylene blue adsorbed or retained in the adsorbents against contact time for three different sizes of adsorbents in 32mg\l, 16mg\l, 8mg\l, and 4mg\l dye solutions respectively. The plots show that there was a steep rise of the curves within the first 20 minutes of contact time, showing that there was maximum adsorption between 0 and 20 minutes. This has been attributed to the availability of enough unoccupied pores into which the adsorbent penetrate and adhere to. The initial curved portions may be attributed to the

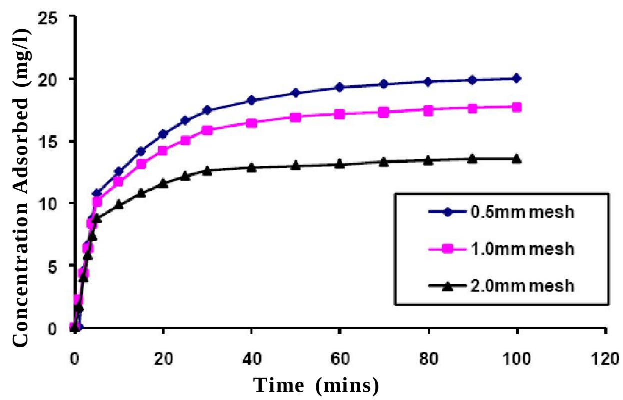

Figure 2 : Plot of contact time against concentration adsorbed for 32 mg/l dye solution across 3 mesh sizes

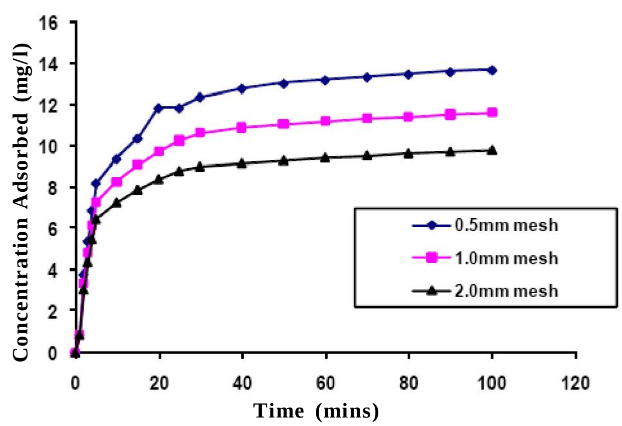

Figure 3 : Plot of contact time against concentration adsorbed for 16 mg/l dye solution across 3 mesh sizes

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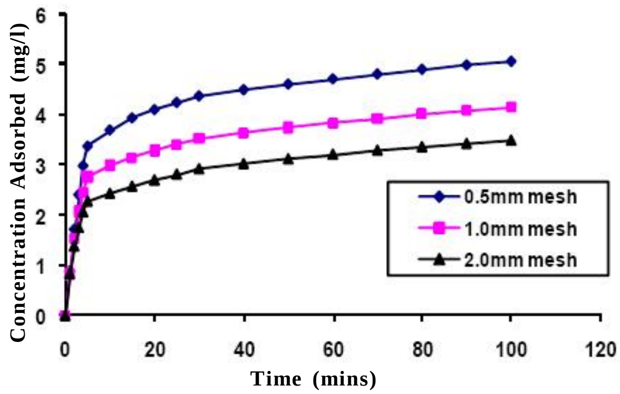

Figure 4 : Plot of contact time against concentration adsorbed for 8 mg/l dye solution across 3 mesh sizes

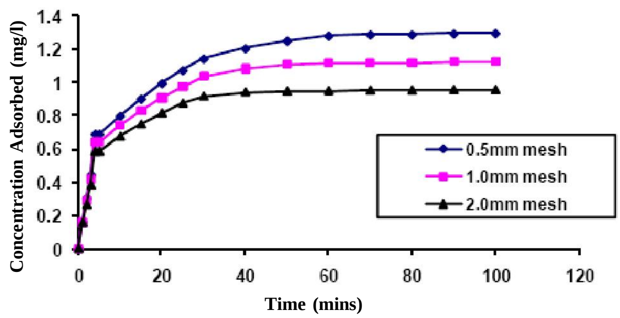

Figure 5 : Plot of contact time against concentration adsorbed for 4 mg/l dye solution across 3 mesh sizes

boundary layer diffusion effect, while the final linear portions may be due to intra particle diffusion effects[28]. Although the comparison between published results should be made carefully, since there are some experimental variables to take into account, like gas flow and type of furnace, that have influence on the final product[16], similar results have been reported[29]. The amount of adsorbent adsorbed increased rather slowly after 50 minutes and finally reaching equilibrium around 100 minutes when the rate of adsorption was equal to the rate of desorption[30].

Effect of particle size

Three adsorbents mesh sizes, 0.5mm, 1.0mm and 2.0mm were used for four different concentrations of the adsorbate. The results in Figures 2-5 show that the 0.5mm sized adsorbent had the highest rate of adsorption with max adsorbed dye concentrations of 19.98mg/l, 13.76mg/l, 5.059mg/l, and 1.29mg/l for 32mg/l, 16mg/l, 8mg/l and 4mg/l respectively, followed by the 1.0mm meshed sized adsorbents with maximum adsorption at 17.69mg/l, 11.61mg/l, 4.15mg/l and 1.12mg/l for 32mg/l, 16mg/l, 8mg/l and 4mg/l dye solutions respectively. The 2.0mm mesh sized adsorbents had the lowest rate of adsorption having maximum dye adsorptions of 13.5mg/l, 9.79mg/l, 4.15mg/l and 0.9mg/l for the 32mg/l, 16mg/l, 8mg/l and 4mg/l adsorbate dye solutions respectively. The above observation has been attributed to the fact that there is an increase in surface area of the adsorbent with decrease in size. Similar observations had been reported in our previous works[30,31].

Effect of initial concentration of methylene blue

Four different concentrations of the adsorbate solution were used to investigate the effect of concentration on the removal of methylene blue using activated carbon from *Irvingia Gabonensis* and the results (Figures 2 to 5) show that the amount of adsorbate adsorbed is dependent on the initial concentration of the adsorbate solution. This is illustrated with adsorption process using 0.5mm particle sized carbon as shown in TABLE 1. The percentage adsorption of the dye was calculated using equation 2.

% adsorption = [Co–C/Co] x 100 (2)

where Co is the Initial dye concentration and C the final dye concentration (mg/l).

TABLE 1 : Effect of initial concentration of methylene blue on % adsorbed

Sr. No.	Initial Dye Conc.(mg/l)	Dye Adsorbed (mg/g)	% Adsorption
1	32	9.99	62.44
2	16	6.88	86.00
3	8	2.53	63.13
4	4	0.65	32.25

It is evident from the table that the amount of dye retained by the adsorbents increased with increase in initial dye concentration[32] up to 16mg/l of dye concentration. The concentration provides an important driving force to overcome all mass transfer resistance of the dye between the aqueous and solid phases[33]. Further increase in the initial concentration of the dye solution led to a decrease in the percent of dye removed from the solution. This is as a result of the fact that at higher concentrations, lower adsorption yields were observed because of the saturation of the adsorption sites[21].

Sorption isotherm studies

The Langmuir and Freundlich isotherm models were used to estimate the adsorption intensity of the sorbent towards the adsorbate solutions for the three different adsorbent sizes in $50cm^3$ of the 32mg/l adsorbate dye solution. The plots in Figures 6 and 7 shows that the results fitted into the two isotherm models employed at average R^2 values of 0.8817 and 0.9766 for Langmuir and Fruendlich isotherms respectively, though the adsorption process was better described by the Fruendlich isotherm. Özer and Dursun[34] had reported that adsorption data from their study involving the removal of methylene blue from aqueous solution by dehydrated wheat bran carbon were well described by the Langmuir model, although they could be modelled by the Freundlich and Redlich-Peterson model as well. Abd El-Latif et al reported that methylene blue adsorption fitted better in Freundlich isotherm for hydrolyzed oak sawdust[32].

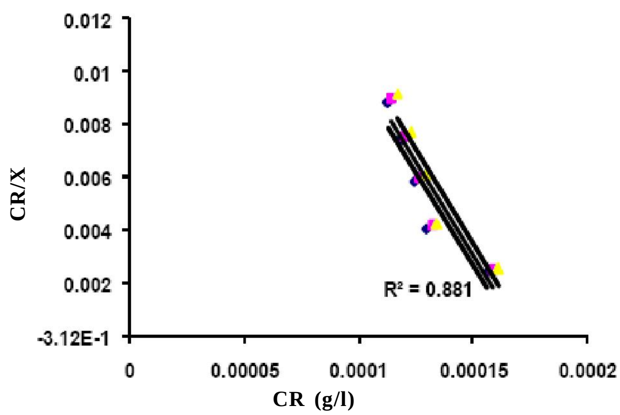

Figure 6 : Langmuir isotherm plot

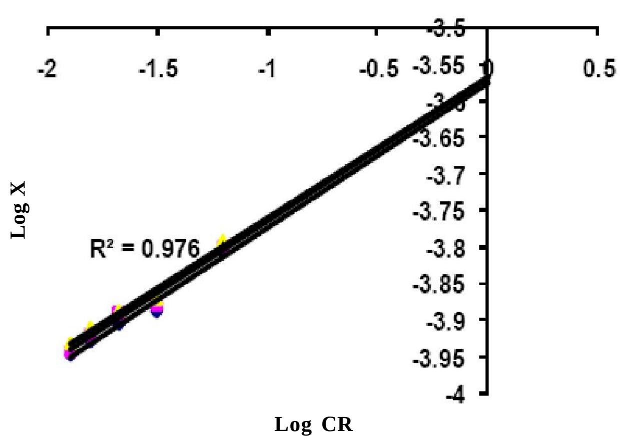

Figure 7 : Freudlich isotherm plot

CONCLUSION

Irvingia Gabonensis a natural waste material was used in the production of activated carbon which was found to be very effective in the remediation of effluent dye infested water, recording maximum percentage adsorption of 85% with 0.5mmmesh sized adsorbent in 16mg/l dye solution. We may conclude that the seed shell has therefore added to the growing list of agricultural waste materials that could be used as adsorbents in treating waste waters.

REFERENCES

[1] M.Balakrishan, S.Arul Antony, S.Gunasekeran, R.K.Natarajan; Indian J.Sci.Technol., **1(7)**, 1 **(2008)**.

[2] O.Yavuz, A.H.Aydin; Polish J.of Environ.Stud., **15(1)**, 151 **(2006)**.

[3] M.M.Alkan, Y.Onganev; Water Air Soc.Pollut., **120**, 229 **(2000)**.

[4] A.El Nemr, O.Abdelwahab, A.El-Sikaily, A.Khaled; J.Hazard Matter, **16(1)**, 102 **(2009)**.

[5] K.V.S.Kumar, V.Ramamurthi; E-Journal of Chemistry, **6(R)**, 621 **(2004)**.

[6] A.Ould-Idriss, M.Stitou, E.M.Cuerda-Correa, C.Fernández-González, A.Macías-García, M.F.Alexandre-Franco, V.Gómez-Serrano; Fuel Processing Technol., **92**, 261 **(2011)**.

[7] T.Santhi, S.Manonmanu, T.Smitha; Intl.J.of Engineering Sci.and Technol., **2(3)**, 287 **(2010)**.

[8] I.F.Odesola, N.O.Daramola; Am.J.Sci.Ind.Res., **1(2)**, 332 **(2010)**.

[9] C.Namasivayam, K.Kadirvelu; Bioresource Technol., **48**, 79 **(1994)**.

[10] G.Sun, X.Xu; Ind.Eng.Chem.Res., **36**, 808 **(1997)**.

[11] B.Chandran, P.Nigam; Environ.Intl., **28**, 29 **(2002)**.

[12] V.Vadivela, V.K.Kumar; J.Colloid Interface Sci., **286**, 90 **(2005)**.

[13] R.X.Zhang, H.S.Y.Liu, B.Liu; Bioresources Technol., **98**, 1319 **(2007)**.

[14] T.Santhi, S.Manonmani, D.Smitha, K.Mahalakshmi; J.Hazard.Mater, **179(1-3)**, 178 **(2010)**.

[15] T.D.Rhokhlora, Y.S.Nikitin, A.L.Destistova; Adsorption Sci.Technol., **15(15)**, 333 **(1997)**.

[16] J.M.V.Nabais, C.E.C.Laginhas, P.J.M.Carrott, M.M.L.Ribeiro-Carrott; Fuel Processing Technology, **92**, 234 **(2011)**.

[17] N.Kato, M.Arai, Y.Sakai, J.Mitamura, F.Takahashi; Nippon Kagaku Kaishi, **1**, 11 **(2001)**.

[18] S.T.Pollard, G.D.Fowler, C.J.Sollar, R.Perry; Sci. Total Environ., **116**, 31 **(1992)**.

Full Paper

[19] I.D.Mall, S.N.Upadhyam, V.C.Sharma; Intl.J. Environ.Stud., **51**, 77 **(1996)**.

[20] S.E.Baily, T.J.Olin, R.M.Bricka, D.D.Adrian; Water Research, **33(11)**, 2469 **(1999)**.

[21] A.S.Alzaydien; American Journal of Environmental Sciences, **5(3)**, 197 **(2009)**.

[22] K.G.Bhattacharya, A.Sharma; Dyes Pigm., **65**, 51 **(2005)**.

[23] A.I.Okoye, P.M.Ejikeme, O.D.Onukwuli; Intl.J. Environ.Sci.Tech., **7(4)**, 793 **(2010)**.

[24] A.E.Ochonogor, P.M.Ejikeme; J.Chem.Soc.Nig., **30(2)**, 91 **(2005)**.

[25] American Standard for Testing of Materials International; Method, D2866, **(1994)**.

[26] K.Qureshi, I.Bhatti, R.Kazi, A.K.Ansari; World Academy of Sci.Engineering and Technol., **34**, 194 **(2007)**.

[27] M.Ahmedna, W.E.Marshall, R.M.Rao; Bioresource Technol., **71(2)**, 113 **(2000)**.

[28] R.P.Kumar, S.Varanasi, V.Purushothaman; Indian J.Sci.Technol., **3(1)**, 7 **(2010)**.

[29] C.Troca-Torrado, M.Alexandre-Franco, C.Fernándes-González, M.Alfaro-Domínguez, V.Gómez-Serrano; Fuel Processing Technol., **92**, 206 **(2011)**.

[30] P.M.Ejikeme, A.E.Ochonogor; J.Chem.Soc.Nig., **33(1)**, 132 **(2008)**.

[31] O.C.Okpareke, I.I.Agha, P.M.Ejikeme; J.Chem. Soc.Nig., **26(1)**, 117 **(2010)**.

[32] M.M.Abd El-Latif, Amal M.Ibrahim, M.F.El-Kady; J.of American Sci., **6(6)**, **(2010)**.

[33] M.Do˘gan, M.Alkan, O.Demirbas, Y.Ozdemir, C.Ozmetin; Chem.Eng.J., **124**, 89 **(2006)**.

[34] A.Özer, G.Dursun; J.Hazardous Materials, **146(1-2**), 262 **(2007)**.